Adsorption and dissociation of hydrogen molecules on bare and functionalized carbon nanotubes

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We investigated interaction between hydrogen molecules and bare as well as functionalized single-wall carbon nanotubes (SWNT) using first-principles plane wave method. We found that the binding energy of the H_2 physisorbed on the bare SWNT is very weak, and can be enhanced neither by increasing the curvature of the surface through radial deformation, nor by the coadsorption of Li atom that makes the semiconducting tube metallic. Though the bonding is strengthened upon adsorption directly to Li atom, yet its nature continues to be physisorption. However, the character of the bonding changes dramatically when SWNT is functionalized by the adsorption of Pt atom. Single H_2 is chemisorbed to Pt atom on the SWNT either dissociatively or molecularly. If Pt-SWNT bond is weakened either by displacing Pt from bridge site to a specific position or by increasing number of the adsorbed H_2, the dissociative adsorption of H_2 is favored. For example, out of two adsorbed H_2, first one can be adsorbed dissociatively, second one is chemisorbed molecularly. The nature of bonding is weak physisorption for the third adsorbed H_2. Palladium also promotes the chemisorption of H_2 with relatively smaller binding energy. Present results reveal the important effect of transition metal atom adsorbed on SWNT and advance our understanding of the molecular and dissociative adsorption of hydrogen for efficient hydrogen storage.

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I. INTRODUCTION

Fuel cells have been a real challenge for clean and efficient source of energy in diverse fields of applications with different size and capacity range. Once hydrogen molecule is chosen as potential fuel, its storage, easy discharge for consumption and dissociation into hydrogen atoms to complete the current cycle in the fuel cell to produce the desired electromotive force involve several problems to be solved. Dillon *et al.*[1] have pioneered the idea that carbon nanotubes can be efficient, cheap and rechargeable storage medium for small-scale fuel cells by estimating 5-10 weight percent (*wp*) H_2 adsorption in single-wall carbon nanotubes (SWNT). Later, Ye *et al.*[2] and Liu *et al.*[3] obtained H_2 storage capacities of 8.2 and 4.2 *wp*, respectively. Unfortunately, recent studies further exploring this idea have come up with controversial conclusions[4,5,6,7,8,9]. In the mean time, adsorption of alkali atoms on SWNTs have been proposed to enhance the H_2-uptake[9,10]. Nevertheless, carbon nanotubes have high surface-volume ratio and their functionalization to render them feasible for hydrogen storage through coverage of suitable adatoms has remained to be explored.

In this paper[11], we addressed following questions in order to clarify controversial issues related to the storage of hydrogen molecule on carbon nanotubes: Can H_2 molecule be adsorbed on the SWNT? What is the nature and strength of the bonding? Can the strength of the bonding be modified either by changing the curvature of the surface or by the coadsorption of metal atoms? In particular, can the H_2-uptake on SWNTs be promoted by their functionalization through transition elements? How can H_2 molecule be dissociated? To answer all these questions we investigated the interaction between H_2 molecule and bare, radially deformed and foreign atom adsorbed SWNTs by carrying out calculations within Density Functional Theory (DFT)[12]. Our results not only advance our understanding of H_2 adsorption on carbon nanotubes, but also suggest new ways for efficient hydrogen storage for rapidly growing research on fuel cells.

Our calculations have been carried out using first-principles plane wave method and ultrasoft pseudopotentials[13,14] within Generalized Gradient Approximation (GGA)[15]. Adsorption and dissociation of H_2 is treated within the supercell geometry by optimizing atomic positions. The weak attractive Van der Waals (VdW) interaction becomes crucial in calculating binding energies of weak physisorption bonds, but is not well represented in DFT using GGA[16]. Therefore, in the case of physisorption, weak and attractive VdW interaction energy, E_{VdW}, is obtained from the Slater-Kirkwood approximation[17] using the asymptotic form of the Lifshitz's equation[18]. However, this approach can not be suitable to determine the contribution of VdW interaction in the chemisorption of molecules. In the present calculations we take the zigzag (8,0) SWNT as a prototype tube.

II. ADSORPTION OF H2 ON BARE AND RADIALLY DEFORMED SWNT

To clarify whether H_2 can form stable bonding on the outer or inner surface of a SWNT, we calculated the chemical interaction energy between H_2 and the outer
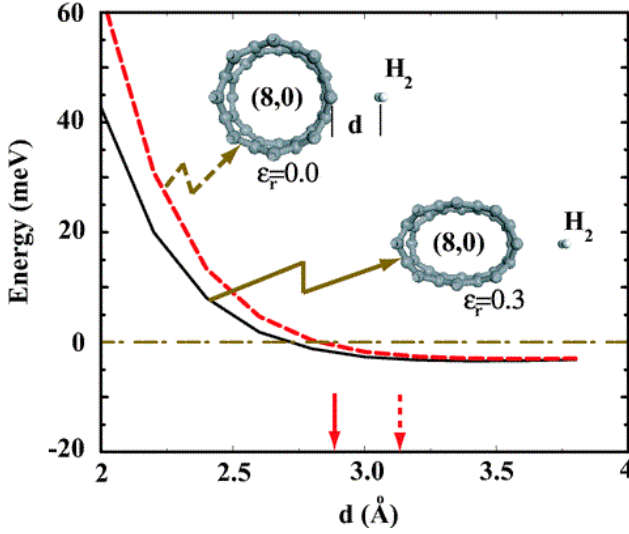
FIG. 1: Variation of chemical interaction energy E_C between SWNT and H_2 molecule as a function of distance d between them. Two cases, namely adsorption to bare and radially deformed SWNT are shown by dashed and continuous lines, respectively. In calculating both curves, atomic structures corresponding to $d \to \infty$ have been used without relaxation. Dash-dotted line indicate zero of chemical interaction energy. Optimized distance for two cases are indicated by arrows.
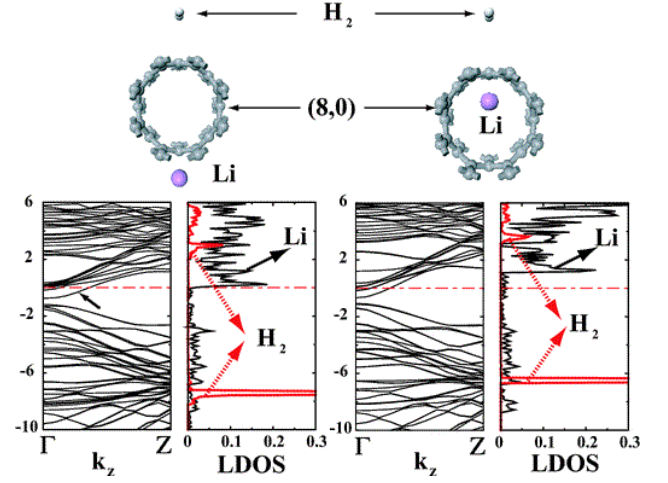

FIG. 2: Atomic configuration, energy band structure and local density of states (LDOS) calculated for the coadsorption of H_2 molecule and single Li atom. Two cases correspond to Li atom chemisorbed on the external and internal surface of the (8,0) zigzag SWNT. Zero of energy is set at the Fermi level, E_F. LDOS calculated at Li and H_2 are shown by continuous and dotted lines, respectively. Metallized SWNT bands are indicated by arrows.

surface of the (8,0) SWNT at different sites (i.e. H-site, above the hexagon; Z- and A-site above the zigzag and above the axial C-C bonds; T-site, a bridge site between two adjacent zigzag C-C bonds) as a function of spacing d. The chemical interaction energy is obtained from the expression, $E_C(d) = E_T[H_2 + SWNT, d] - E_T[SWNT] - E_T[H_2]$, in terms of the total energies of bare nanotube ($E_T[SWNT]$), free H_2 ($E_T[H_2]$), and H_2 attached to SWNT at a distance d ($E_T[H_2 + SWNT, d]$). Here $E_C < 0$ corresponds to an attractive interaction. The stable binding occurs at the minimum of $E_C(d) + E_{VdW}(d)$, the negative of it is denoted as the binding energy E_b. The binding is exothermic when $E_b > 0$. In Fig. 1 we show the variation of $E_C(d)$ calculated for unrelaxed atomic structures at the H-site. Once the atomic structure of both SWNT and H_2 molecules are relaxed the mimimum value of $E_C(d)$ is found to be -27 meV at $d_0 = 3.1$Å at the H-site. Minimum values of $E_C(d)$ calculated for A-, Z-, and T-sites are also very small and comparable to that of H-site. The long range VdW interaction energy calculated for the H-site at d_o is $E_{VdW} \sim$-30 meV. Then the binding energy associated with H_2 molecule adsorbed at H-site is calculated to be $E_b \sim$57 meV. This is a small binding energy and indicates physisorption.

Previous studies[4,5] revealed that the physisorption of individual H_2 molecules with $E_b > 0$ cannot occur on the inner wall of SWNT. Hydrogen molecules prefer to stay either at the center of the tube or to form some cylindrical shells inside depending on radius of the tube. Owing to increased H-H interaction at high coverage, even the

atomic hydrogen cannot form stable structure when it is adsorbed to the inner wall of small radius tube. For (8,0) tube we found that H_2 is trapped and stabilized at the center of the tube with a repulsive interaction energy $E_C = +0.34$ eV. The implementation of H_2 inside the tube having radius in the range of 3 Å is expected to be hindered by this repulsive interaction.

Earlier it has been shown that binding energy of foreign atoms adsorbed on SWNT increase with increasing curvature[19]. Tada et al.[20] have argued that the potential barrier associated with the dissociative adsorption of H_2 on SWNT is lowered with increasing curvature of the tube. It has been proposed that the potential barrier for the dissociation of H_2 adsorbed in the interstitial region between tubes can be lowered by applying radial deformation to the rope or SWNT[21]. It is known that under radial deformation the circular cross section changes and consequently the curvature varies at different locations on the surface. Motivated with those effects of curvature, we examine whether the attractive interaction energy E_C can be enhanced by changing the curvature of the tube via radial deformation. Radial deformation is realized by pressing the tube between two ends of a given diameter. It, in turn, changes the circular cross section of the bare tube with radius R_o to an elliptical one with major and minor axes $2a$ and $2b$, respectively. The atomic structure of (8,0) tube is optimized under radial strain $\epsilon_r = (R_o - b)/R_o \simeq 0.3$ by fixing row of carbon atoms at the end of minor axis. The deformation is reversible so that the tube goes back to its original, undeformed form upon the release of radial strain[22]. The deformation energy (that is the difference between the total energies of

deformed and undeformed SWNTs) is calculated to be E_D =1.4 eV per unit cell. We examined whether the binding energy of H_2 molecule changes under the radial deformation of SWNT. Figure 1 shows the variation of $E_C(d)$ for H_2 approaching toward the high curvature site of the tube (*i.e.* one end of the major axis) at the H-site. The minimum value of the attractive interaction, E_C is -30 meV and occurs at d_o=2.9 Å. For ϵ_r =0.25, we also obtained very small enhancement of $E_C(d)$. Hence, the effect of curvature on the binding energy of H_2 is negligible due to relatively large d_o. This result also suggests that the physisorption energy does not vary significantly depending on the radius of SWNT. Apparently, the binding of H_2 on the outer surface of SWNT is weak and corresponding physisorption energy is small. The binding cannot be enhanced by increasing the curvature locally through radial deformation. Curvature effect or radial deformation may be significant at small d when H_2 is forced towards SWNT surface.

III. COADSORPTION OF HYDROGEN MOLECULE AND LITHIUM ATOM ON SWNT

Next, we examine whether the binding of H_2 is enhanced by the coadsorbed foreign atoms. To this end we first consider Li atom adsorbed on the (8,0) SWNT, since the adsorption of an alkali atom has been proposed to enhance the H_2-uptake[9,10]. Li atom is chemisorbed at the H-site, 1.5 Å above the surface of SWNT with a binding energy of 0.8 eV. Self-consistently calculated electronic structure shown in Fig. 2 reveals that chemisorbed Li atoms donate their 2s-valence electrons to the lowest conduction π^*-band so that the semiconducting (8,0) SWNT (having band gap E_g =0.6 eV) becomes metallic. This is a behavior common to the other alkali atoms adsorbed on SWNTs[23]. In order to examine the indirect effect of coadsorbed Li we considered H_2 as attached at the opposite site to Li. The optimized structure of the physisorbed H_2 is shown in Fig. 2 together with relevant structural parameters. We found E_C has a minimum value of -35 meV at d_o =3.4 Å. Similar study has been also performed for Li atom adsorbed on the inner wall of SWNT while H_2 is on the external wall directly above the coadsorbed Li as shown in Fig. 2. In this adsorption configuration minimum value of E_C practically did not change. The local density of states calculated on Li atom and H_2 refuse the possibility of any significant interaction between adsorbates. As a result, our calculations for both external and internal adsorption of Li rule out any indirect effect of coadsorbed Li to enhance the binding of H_2 on SWNT. The occupation of empty conduction band by the alkali electrons and hence metallization of SWNT did not affect the bonding of H_2. These results are in agreement with the first principles calculations by Lee *et al.*[26]. However, the effect of Li on the adsorption of H_2, whereby H_2 is attached directly to Li atom is found significant. The minimum value of E_C has increased to -175 meV, while
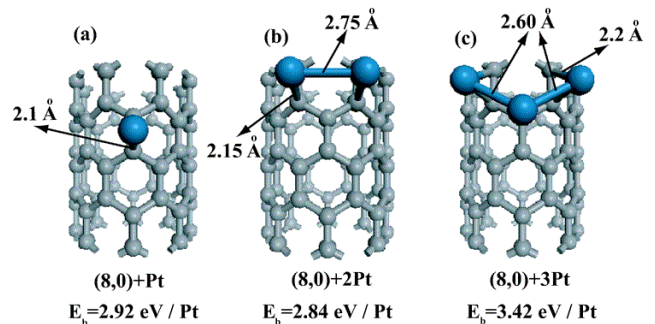

FIG. 3: (a) Atomic configurations for single, double and triple Pt atoms adsorbed on the (8,0) SWNT. Average binding energy of adsorbed Pt atoms E_b and bond distances are indicated.

d_o decreased to 2.1 Å. Briefly, the coadsorption of Li does not have any indirect effect on the binding of H_2, but the energy associated with direct binding to Li is enhanced. However, the nature of bonding remains physisorption in direct and indirect cases.

IV. COADSORPTION OF HYDROGEN MOLECULE AND PLATINUM ATOM ON SWNT

A single transition metal atom adsorbed on the outer surface of SWNT has shown interesting properties, such as high binding energy and magnetic ground state with high net magnetic moment. For example, transition element atoms (Ti, V, Cr, Mn, Fe, Co, Pt, *etc.*) have crucial adsorption states on nanotubes[23] and some of them (Ti, Ni, Pd) form continuous or quasi-continuous metal coating on the SWNT[24,25]. As for Pt atom, it is known to be a good cathalist in various chemical processes. While SWNTs offer high surface/volume ratio, the interaction between H_2 and Pt atom adsorbed on SWNT may be of interest. Now we investigate the character of the bonding between H_2 and Pt adsorbed on SWNT and address the question of how many H_2 molecules can be attached to an adsorbed Pt atom and how strong is the binding.

A. Adsorption of Pt atoms on SWNT

We first examine the adsorption of Pt atom(s) on (8,0) SWNT. The character of the bonding has been investigated by placing Pt atoms on the A-sites of (8,0) tube (that is known to yield highest binding energy[23]) and then by optimizing the structure. Three different adsorption configuration have been examined, namely one, two and three Pt atoms adsorbed on the adjacent sites to represent a small cluster on SWNT as described in Fig. 3. Calculated binding energies of Pt atoms have increased as the number of Pt atoms increases from one to three in the same neighborhood. On the other hand, the C-Pt distance gradually increases with increasing number
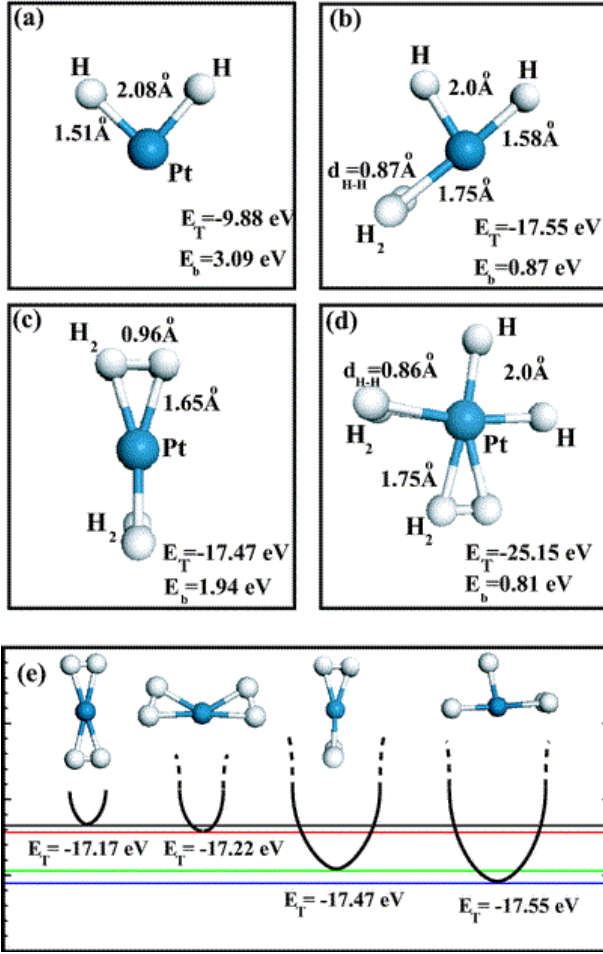
FIG. 4: Optimized binding configuration of H_2 molecules adsorbed to a free Pt atom. (a) Dissociative adsorption of a single H_2 molecule. (b) The first H_2 is dissociatively, second H_2 molecularly adsorbed. (c) Two H_2 are molecularly adsorbed. (d) Two H_2 are molecularly, one H_2 dissociatively adsorbed (e) Four different configurations related with the adsorption of two H_2 to the same free Pt atom and corresponding four minima on the Born-Oppenheimer surface described schematically. Binding energy of each adsorbed additional hydrogen molecule E_b, total energy with respect to constituent atoms E_T and bond distances are indicated.
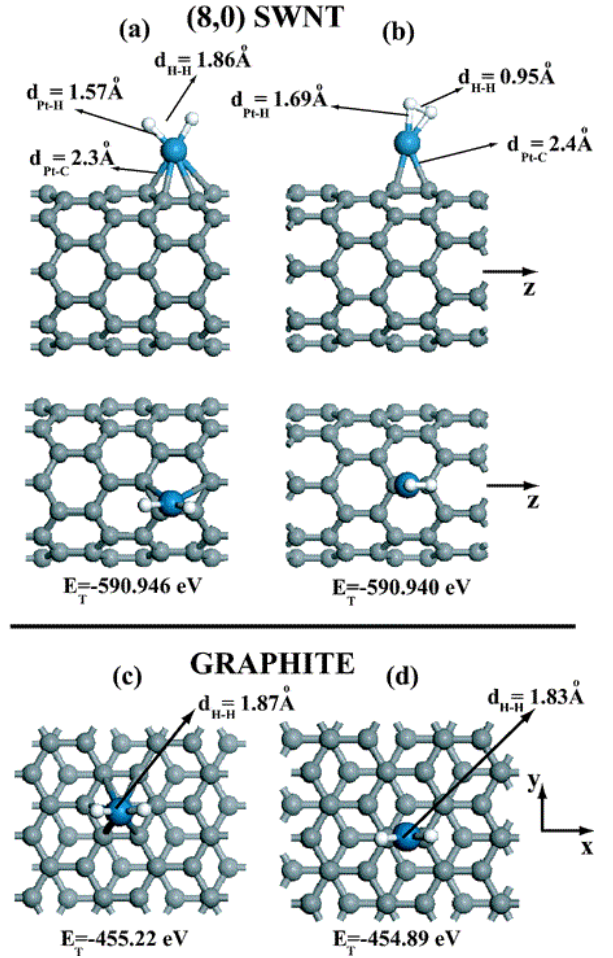
FIG. 5: Optimized adsorption geometry of H_2 molecule on a single Pt atom. (a) Pt atom is adsorbed near the H-site of (8,0) SWNT (side and top view) (b) Pt at the A-site (bridge position) of (8,0) SWNT (side and top view) (c) Pt atom is adsorbed near the H-site of the graphite surface (d) Pt atom at the A-site of graphite. E_T is the total energy relative to the constituent C, Pt and H atoms.

of Pt atoms adsorbed in the same neighborhood. This paradoxical situation can be understood by the increasing Pt-Pt coupling, which happens to be comparable to C-Pt coupling derived by the Pt-3d and C-2p orbitals.

B. Adsorption of H2 to a free Pt atom

We now consider the interaction between H_2 molecules and a free Pt atom. Optimized binding structures are shown in Fig. 4. Upon approaching to a free Pt atom, single H_2 molecule dissociates and form PtH_2 with Pt-H bond distance d_{Pt-H}=1.51 Å and d_{H-H}=2.08 Å. The total energy E_T relative to the energies of free Pt and H

atoms is calculated -9.88 eV. The binding energy relative to H_2 molecule and free Pt atom is E_b=3.09 eV. As for the adsorption of H_2 to PtH_2, there are several minima on the Born-Oppenheimer surface: The first minimum corresponds to a configuration in Fig. 4(b) where PtH_2 preserves the dissociated configuration while second H_2 is molecularly adsorbed. Even if H-H interaction of adsorbed H_2 is weakened and hence the H-H distance has increased to 0.87Å, we identify it as molecular adsorption. We denote this configuration as PtH_2+H_2. The adsorbed H_2 molecule is perpendicular to the plane of PtH_2. The binding energy of the second H_2 to PtH_2 is calculated to be E_b=0.87 eV. Under these circumstances the average binding energy of each H_2 is 1.98 eV. In the second configuration, identified as Pt-2H_2 as shown in Fig. 4(c), both H_2 are molecularly adsorbed. As H-H molecular bonds are weakened, d_{H-H} is increased to 0.96Å and all Pt-H bonds have uniform length with d_{Pt-H} =1.65Å. Here ad-

sorbed H_2 molecules are perpendicular. The binding energy of each molecules is calculated to be 1.94 eV slightly less then the average binding energy in $PtH+H_2$ configuration. The configuration PtH_2+2H_2 shown in Fig. 4(d) involves the adsorption of three H_2 molecules; one dissociatively, remaining two are molecularly adsorbed. Here Pt-H_2 planes of two molecularly adsorbed H_2 are perpendicular. The binding energy of the third H_2 relative to the energy of PtH_2+H_2 in Fig. 4(b) is found to be 0.81 eV. Accordingly, the average binding energy of each H_2 is 1.6 eV relative to free H_2 and free Pt atom. Fig. 4(e) compares four distinct configurations related with the adsorption of two molecules on the same free Pt atom. It appears that these configurations correspond to local minima on the Born-Oppenheimer surface and the configuration in Fig. 4(b) appears to have lowest energy.

C. Adsorption of H2 to a Pt atom on SWNT

We deduced two configurations for the adsorption of a single molecule to a Pt atom adsorbed on the (8,0) SWNT as described in Fig. 5. While these two chemisorption configuration look dramatically different, their total energies differ only by 6 meV (that is smaller than the accuracy range of DFT). In the configuration described in Fig. 5(a) H_2 is dissociatively adsorbed with binding energy E_b=1.1 eV relative to free H_2 and Pt adsorbed on SWNT, i.e. $E_T[H_2]$ and $E_T[Pt+SWNT]$, respectively. The H-H and Pt-H distances are 1.86 Å and 2.3 Å, respectively. Whereas in the configuration in Fig. 5(b) H_2 is molecularly adsorbed with a significantly weakened H-H bond. H_2 approaching from different directions and angles results in a chemisorption state with binding energy E_b =1.1 eV and Pt-H distance 1.7 Å. The length of H-H bond has increased from 0.75 Å to 0.95 Å upon adsorption[27]. Whereas, this configuration appears to be less energetic than the former one, the energy difference between them is only 6 meV. Notably, while in the first configuration leading to dissociative adsorption Pt atom is located near hollow H-site, in the "molecular" adsorption of H_2 Pt atom is adsorbed at the A-site. As compared to the average binding energy calculated for H_2 adsorption to a free Pt atom, the molecular adsorption of H_2 to Pt atom adsorbed on SWNT is relatively weaker due to the Pt-SWNT bond.

Adsorption of H_2 to a single Pt atom attached to the surface of graphite is of interest in order to reveal how the binding energy and binding configuration of H_2 depends on the radius of SWNT. We considered two configuration, namely single Pt atom is adsorbed near hollow H-site, as shown in Fig. 5(c) and Pt at the A-site as shown in Fig. 5(d). For both location of Pt atom on the graphite surface, H_2 molecule approaching the adsorbed Pt atom is dissociated and eventually Pt atom formed two Pt-H bonds with individual H atoms. In this case the binding with the graphite surface is weaker than that on SWNT, and thus d_{Pt-C} is increased to 2.4Å. Relatively
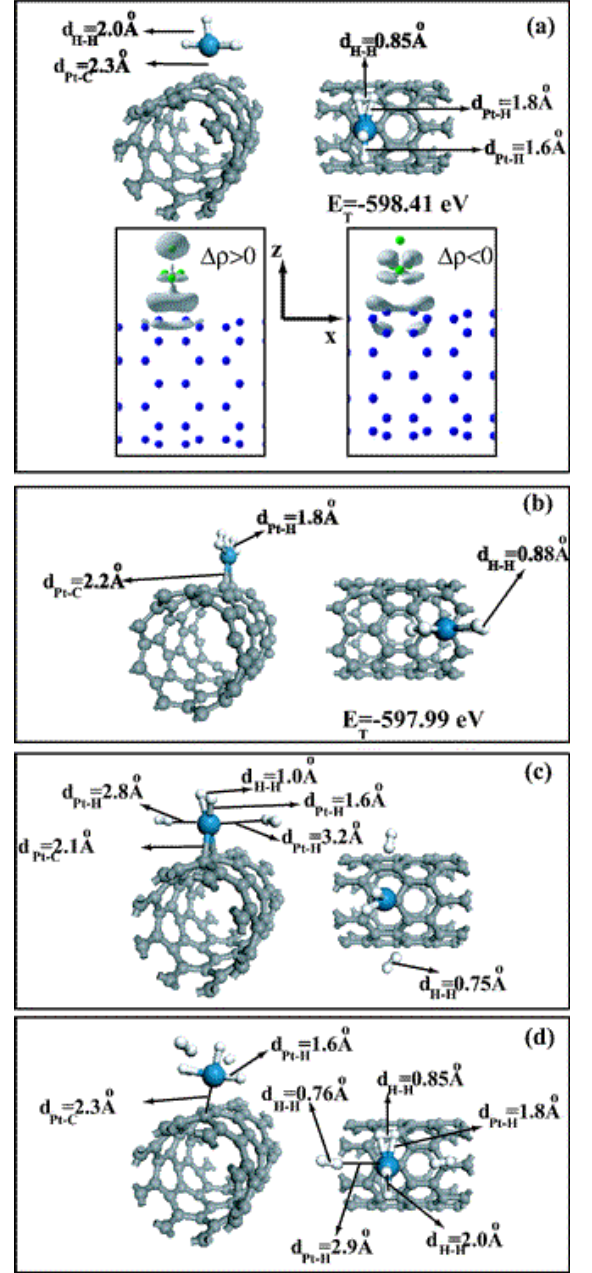

FIG. 6: Optimized structure of H_2 molecules adsorbed to the Pt atom on the SWNT. (a) One H_2 adsorbed to PtH_2. The inset show the regions of charge depletion ($\Delta\rho < 0$) and charge accumulation ($\Delta\rho > 0$) as a result of the bonding between SWNT and PtH_2+H_2 in (a). (b) Another local minima where two H_2 is molecularly adsorbed to the Pt atom. (c) One H_2 is chemisorbed two H_2 are weakly bound. (d) four H_2.

weaker interaction between Pt and graphite surface allows stronger interaction between H_2 and Pt, as in the case of free Pt atom, and hence leads to the dissociation of the molecule. In view of two limiting case in Fig. 5, one can expect that dissociation of H_2 may occur for SWNTs having larger R.
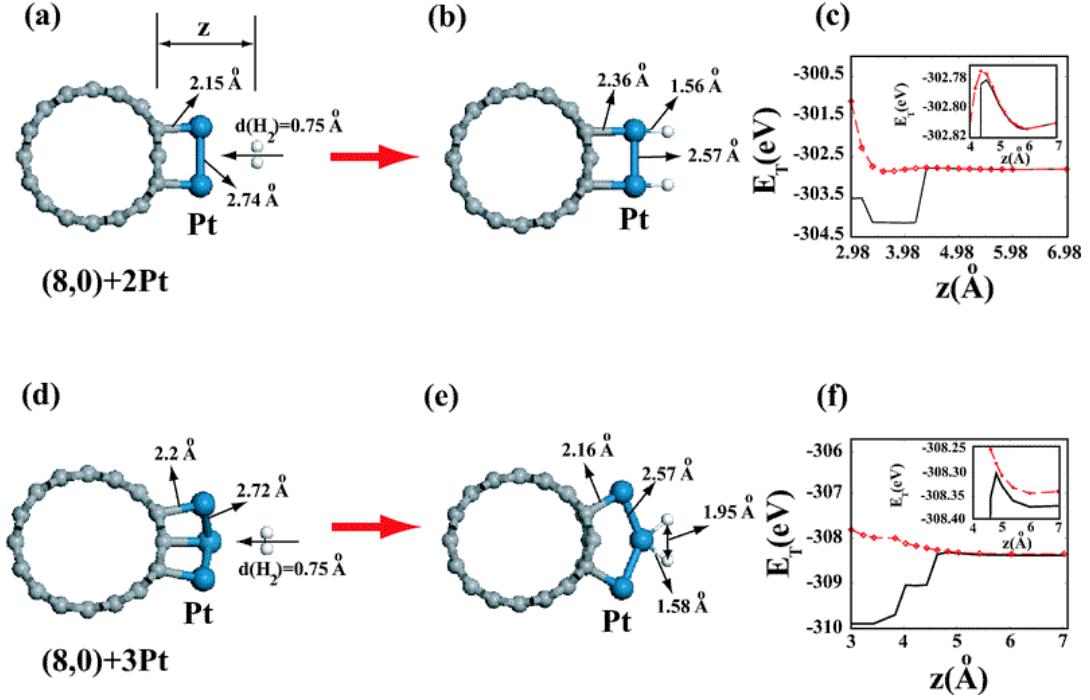
FIG. 7: Dissociative adsorption of single H_2 on a small Pt cluster adsorbed on SWNT (a). One H_2 is approaching two adjacent Pt atoms adsorbed on SWNT. (b) Optimized geometry after dissociative adsorption of H_2. (c) Variation of total energy with distance z. Small circles corresponds to E_T for unrelaxed H_2 and unrelaxed SWNT. Dotted curve corresponds to E_T of the geometry relaxed at certain distances. (d), (e) and (f) same as (a), (b) and (c) except the Pt cluster consists of 3 Pt atoms. z is the distance from the surface of SWNT. Variation of $E_T(z)$ is amplified by inset.

To answer the questions of how many H_2 molecule can be attached to a single Pt atom we perform a systematic study outlined in Fig. 6. First we let a second H_2 approaches to Pt atom on SWNT that already has one H_2 molecule attached as in Fig. 5(b). The final optimized geometry of Pt and adsorbed H_2 molecules in Fig. 6(a) is similar to the configuration $PtH_2 + H_2$ described in Fig. 4(b). This situation is explained by the weakening Pt-C bond between PtH_2 and SWNT shown in Fig. 5(a) which is followed by the increase of d_{Pt-C}. First H_2, which was initially chemisorbed to Pt as a molecule has dissociated upon the molecular adsorption of the second H_2. The dissociation of H_2 is an indirect process and is mediated by the weakening of the Pt-C bonding through the molecular adsorption of second H_2. The difference charge density $\Delta\rho(\mathbf{r}) = \rho_T(\mathbf{r}) - \rho_{SWNT}(\mathbf{r}) - \rho_{PtH_2+H_2}(\mathbf{r})$ calculated from the difference of total charge density $\rho_T(\mathbf{r})$ of SWNT+PtH_2+H_2 in Fig. 6(a) and those of SWNT and PtH_2+H_2 indicates that while the charge of Pt-d_{xy} and C-$p_{x,y}$ orbitals are depopulated, the Ptd_{z^2} and C-p_z orbitals become populated to form Pt-SWNT bond. This result suggests that in a reverse situation the weakening of the Pt-SWNT bond would lead to the transfer of charge from Pt-C bond to Pt-H bonds resulting in increased population of d_{xy}-orbitals in favor of the dissociation. Interestingly, exactly the same configuration has been obtained even when two H_2 molecule approach concomitantly the bare Pt adsorbed on SWNT. Another

configuration related with two molecularly adsorbed H_2 is shown in Fig. 6(b), which appears to be a local minima on the Born-Oppenheimer surface and $\sim$0.4 eV less energetics than that in Fig. 6(a). The configuration of Pt+2H_2 has remained even after SWNT is removed.

In Fig. 6(c), two H_2 approaching from both sites of PtH_2 already adsorbed on SWNT have been attached by weak physisorption bonds resulting PtH_2+2H_2. Their distances to Pt atom are relatively larger (2.1Å and 3.2Å) than that occurred for molecularly chemisorption of H_2. The latter Pt-H_2 distance is too long and the binding energy is $\sim$ 20 meV; the binding energy can increase slightly by the VdW interaction but the adsorbed molecule can desorb and escape from Pt at high-temperature. Note that due to weak interaction between PtH_2 and both H_2 molecules, the Pt-C bond becomes stronger, and consequently H-H distance of PtH_2 is closed to be associated in H_2. The attempts to attach more than three molecules to the Pt atom have failed. For example, as shown in Fig. 6(d), from four H_2 brought at the close proximity of Pt atom, only three were attached (one dissociatively chemisorbed, one molecularly chemisorbed, one physisorbed and the forth escaped). At the same time the Pt-SWNT bond has weakened and hence d_{Pt-C} distance has increased to 2.3Å. We define the interaction energy between Pt+nH_2, where n=2 (one of H_2 is dissociated), 3 and 4 (one of H_2 is dissociated) and SWNT in Fig. 6(a-c) as $E[Pt-nH_2]+E_T[SWNT]-E_T[Pt+nH_2+SWNT]$. Here

the total energies are calculated using the same atomic structures in Fig. 6(a-c). Calculated interaction energies for each case are 0.68 eV, 1.88 eV and 0.78 eV, respectively. Using the similar procedure we also calculated the interaction energy between Pt+H_2 (where H_2 is molecularly adsorbed) and SWNT in Fig. 5(a) to be 1.93 eV. Note that the variation of these energies with structure and Pt-C distances confirm the above arguments related with the dissociation of one of H_2 followed by the weakening of the bond between Pt and SWNT.

D. Adsorption of H2 to a small Pt cluster on SWNT

As shown in Fig. 7(a), the situation is different in the case of interaction between H_2 and a small Pt cluster (consisting of a few Pt atoms adsorbed at close proximity). As H_2 approaches two Pt atoms on SWNT it starts to dissociate at a distance $\sim$ 3.9Å from the surface of SWNT. The optimized configuration is shown in Fig. 7(b) where H-H molecular bond is broken and each adsorbed Pt atom formed a Pt-H bonds with d_{Pt-H}=1.56Å. Upon chemisorption d_{Pt-C} increased from 2.15Å to 2.36Å. The dissociation process schematically shown in Fig. 7(c) by plotting the variation of total energy E_T as a function of z for two different cases. The curve by small circles corresponds to the total energy of SWNT+Pt_2 and H_2 calculated for different H_2-tube distance z by keeping the atomic configuration at $z \to \infty$ frozen for all z. The continuous curve is obtained by relaxing the atomic configuration at certain values of z. We see that for $z < 4.2$Å E_T starts to lower upon the onset of dissociation. We note very small barrier at about $z \sim 4.5$Å. Upon overcoming this energy barrier, the process is exothermic with an energy gain of $\sim$ 1.2 eV. As described in Fig. 7(d-f), the adsorption of single H_2 on a Pt cluster consisting of three Pt atoms also results in dissociation of the molecule. As the size of cluster increased by inclusion of the third Pt atom, the small potential barrier at $z \sim 4.5$Å is further lowered, the binding energy increased to 1.5 eV. Also one of the Pt atoms which binds both H atom is detaches from the SWNT surface. This situation confirms that Pt-SWNT bonds are weakened upon the (molecular or dissociative) adsorption of H_2 to Pt.

The interaction between Pd atoms adsorbed on SWNT and H_2 molecule is somehow similar to that with Pt atom. However, the latter case leads relatively less strong interaction and smaller binding energies. For example, the interaction between H_2 and a single Pd atom adsorbed on SWNT results in a binding between chemisorption and physisorption with a binding energy of 0.6 eV. In this case, while the H-H bond length is stretched a little from the normal value 0.7 Å to 0.8 Å, the C-Pd bond is stretched from 2.1 Å to 2.2 Å. Small changes after the adsorption of H_2 are manifestations of relatively weak H_2-Pd interaction. In contrast to adsorbed two Pt atom in Fig. 7(a) breaking the H_2 molecule, two adsorbed Pd atoms give rise to chemisorption of molecule with more stretched H-H bonds.

V. CONCLUSIONS

In this work we presented a detailed analysis of the interaction between hydrogen molecule and a SWNT. We found that the binding energy between H_2 and outer surface of a bare SWNT is very weak and the physisorption bond can easily be broken. We showed that the binding of H_2 to the outer surface cannot be enhanced by applying radial deformation to increase curvature effects at the site facing H_2 molecule. In contrast, the interaction between the inner surface of (8,0) tube and H_2 is repulsive which can prevent molecules from entering inside the tube. The repulsive interaction may turn to be attractive for large tube radius. To promote H_2 uptake on SWNT surface we considered functionalized tubes through adsorption of foreign atoms. The binding energy of H_2 on SWNT surface did not increase by the coadsorption of Li. However, the binding energy increased if H_2 is directly attached to adsorbed Li; yet the nature of the bonding remained physisorption.

The situation with Pt atom, which can make strong chemisorption bonds with the outer surface of SWNT is found to be interesting from the point of view of H_2 storage. We showed that H_2 molecule can form chemisorption bonds with free Pt as well as Pt adsorbed on SWNT. Single H_2 adsorbed on a free Pt atom dissociates and forms two strong Pt-H bonds. On the other hand, while single H_2 molecule is molecularly chemisorbed to a single Pt atom at the A-site of SWNT surface, it can dissociate if Pt atom adsorbed near the hollow site. Even the molecular adsorption of single H_2 can turn dissociative if a second H_2 is molecularly adsorbed to the same Pt atom. The dissociative adsorption is mediated by the weakening of Pt-C bonds either due to a specific location of Pt on SWNT or due to the second H_2 molecularly adsorbed to Pt. Dissociative adsorption of single H_2 to a single Pt atom on the graphite surface suggests that the dissociation of H_2 is favored on SWNTs having large radius. Our analysis suggests that single Pt adsorbed on SWNT can bind up to two H_2 molecules with significant binding energy in the chemisorption range. Beyond two adsorbed H_2, additional molecules form weak physisorption bonds with Pt. Single Pd atom adsorbed on SWNT exhibits similar effects but in relatively weaker manner as compared to that of Pt. Interesting interaction between H_2 and Pt and resulting bonding mechanisms justifies similar investigations of SWNTs functionalized by other transition elements (in particular Ti, Ni, Cr, V) for a higher wp H_2 storage.

Acknowledgments

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[1] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature **386**, 377 (1997).

[2] Y. Ye, C.C. Ahn, C. Witham, B. Fultz, J. Liu, A.G. Rinzler, D. Colbert, K.A. Simith, R.E. Smalley, Appl. Phys. Lett. **74**, 16 (1999).

[3] C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, M.S. Dresselhaus, Science **286**, 1127 (1999).

[4] S.M. Lee, Y.H. Lee, Appl. Phys. Lett. **76**, 20 (2000).

[5] Y. Ma, Y. Xia, M. Zhao, and M. Ying, Phys. Rev. B **65**,155430 (2002).

[6] F. Darkrim, D. Levesque, J. Chem. Phys. **109**, 12 (1998)

[7] K.A. Eklund, P.C. Williams, Chem. Phys. Lett. **320**,352 (2000).

[8] M. Siraishi, T. Takenobu, A Yamada, M. Ata, H. Kataura, Chem. Phys. Lett. **358**, 213 (2002).

[9] P. Chen, X. Wu, J. Lin, K.L. Tan, **285**, 91 (1999).

[10] P. Dubot and P. Cenedese, Phys. Rev. B **47**, 208 (1999).

[11] This work is based on Y. Öztürk's M.S. Thesis, Bilkent University 2003 (Unpublished)

[12] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, B864 (1964); W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).

[13] D. Vanderbilt, Phys. Rev. B **41** 7892 (1990).

[14] Numerical calculations have been performed by using VASP package: G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (19930; G. Kress and J. Furthmüller,*ibid* **54**, 11169 (1996).

[15] J. P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackso, M.R. Pederson, D.J. Singh and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[16] W. Kohn, Y. Meir, and D.E. Makarov, Phys. Rev. Lett. **80**, 4153 (1998).

[17] T.A. Halgren, J. Am. Chem. Soc. **114**, 7827 (1992).

[18] E. M. Lifshitz, Zh. Eksp. Teor. Fiz. **29**, 94 (1956); Sov. Phys. JETP **2**, 73 (1956).

[19] O. Gülseren, T. Yildirim, and S. Ciraci, Phys. Rev. Lett. **87**, 116802, (2001).

[20] K. Tada, S. Furuya and K. Watanabe, Phys. Rev. B **63**, 155405 (2001).

[21] S.-P. Chan, G. Chen, X.G. Gong, and Z.-F. Liu, phys. Rev. Lett. **87**, 205502 (2001).

[22] O. Gülseren, T. Yildirim and S. Ciraci, Phys. Rev. B **65**, 155410 (2002); O. Gülseren, T. Yildirim, S. Ciraci and C. Kilic, Phys. Rev. B **65**, 153405 (2002).

[23] E. Durgun, S. Dag, V.K. Bagci, O. Gülseren, T. Yildirim, S. Ciraci, Pyhs. Rev. B **67**, R201401 (2003); E. Durgun, S. Dag, S. Ciraci and O. Gülseren, J. Phys. Chem. B **108**, 575 (2004).

[24] S. Dag, E. Durgun, and S. Ciraci, Phys. Rev. B **69**, 121407(R) (2004); S. Dag and S. Ciraci, Phys. Rev. B (in press)

[25] X. Zhang and H. Dai, Appl. Phys. Lett. **77**, 3065 (2000); Y. Zhang, N. W. Franklin, R. J. Chan and H. Dai, Chem. Phys. Lett. **331**, 35 (2000).

[26] E.-C. Lee, Y.-S. Kim, Y.-G. Jim and K.J. Chang, Phys. Rev. B **66**, 073415 (2002).

[27] Since, the bond distance of H_2 is extended by 20%, the H-H interaction is weaker than that in free H_2. For $d_{H-H} \sim 1$Å the adsorption may be considered as an intermediate stage between molecular and atomic adsorption.